

PROCESS FOR PREPARING ASPARTATES

BACKGROUND OF THE INVENTION

The present invention relates to novel aspartates, a process for preparing them from primary amines and maleates and to their use as reactive components for polyisocyanates in two-component polyurethane coating compositions and for preparing polyurethane prepolymers.

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Two-component coating compositions which contain, as binder, a polyisocyanate component combined with one or more isocyanate-reactive components are known. They are suitable for preparing high quality coatings which are hard, elastic, abrasion resistant, solvent  
10 resistant and weather resistant.

Secondary polyamines which contain ester groups have become established in the two-component surface coating industry. They are particularly suitable, in combination with lacquer polyisocyanates, as  
15 binders in low-solvent or solvent-free, high solids coating compositions because they provide rapid curing of the coatings at low temperatures.

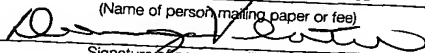
These secondary polyamines are polyaspartates and are described, e.g., in U.S. Patents 5,126,170, 5,214,086, 5,236,741,  
20 5,243,012, 5,364,955, 5,412,056, 5,623,045, 5,736,604, 6,183,870, 6,355,829, 6,458,293 and 6,482,333 and published European Patent Application 667,362. In addition, aspartates containing aldimine groups are also known (see U.S. Patents 5,489,704, 5,559,204 and 5,847,195). Their use as the only isocyanate-reactive component or mixed with other  
25 isocyanate-reactive components in two-component coating compositions are also described in the above-identified patents.

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The process for preparing these polyaspartates is the reaction of the corresponding primary polyamines with maleates or fumarates corresponding to the formula



wherein  $R_3$ ,  $R_4$ ,  $R_5$  and  $R_6$  are identical or different organic groups, resulting in the formation of secondary polyamines. Due to stearic, structural and electronic effects, these secondary amino groups have  
10 sufficiently reduced reactivity towards isocyanate groups to be mixable with polyisocyanates in a reliable and easy manner.

The reaction which is used to prepare polyaspartates is the addition of primary amines to the activated C-C double bond in vinyl  
15 carbonyl compounds, which has been described in the literature (see Chem. Ber. 1946, 38, 83; Houben Weyl, Meth. d. Org. Chemie, Vol. 11/1, 272 (1957); Usp. Chimii 1969, 38, 1933). It has been found, however, that this reaction does not proceed to completion during the course of the actual synthesis process (e.g., 24 hours with stirring at 60°C). The actual  
20 extent of the reaction is dependent upon the type of primary polyamine. Thus, the degree of conversion (measured by the concentration of free, unconverted maleate and fumarate, into which maleate rearranges in the presence of basic catalysts) after 1 day with 1,6-hexanediamine is about 90 to 93%. The degree of conversion after 1 day with a cycloaliphatic  
25 polyamine having sterically hindered primary amino groups, i.e., 4,4'-diamino-3,3'-dimethyldicyclohexylmethane is only 77%. Complete or essentially complete conversion is achieved only after several days or, in the case of 4,4'-diamino-3,3'-dimethyldicyclohexyl-methane, only after several months.

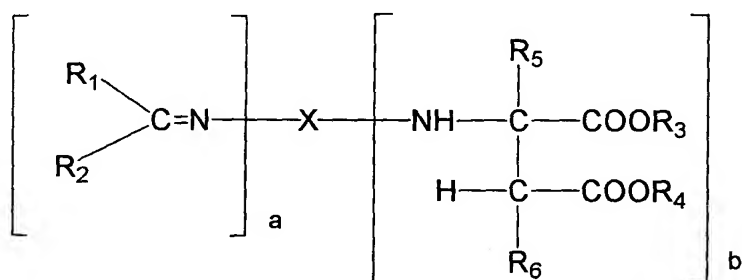
In a typical commercial production, the reaction is run for sixteen hours when the conversion is somewhere between 75 and 95% complete depending on the amine used. The "unfinished" material is drummed and held in storage until the reaction is complete. This typically takes  
 5 anywhere from two weeks to six months.

U.S. Patent 5,821,326 describes the use of certain five-membered aromatic ring compounds as catalyst to accelerate the preparation of the aspartates.

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### DESCRIPTION OF THE INVENTION

The present invention is directed to novel aspartates of the formula:



15 where

X represents an m-valent organic residue obtained by removing the primary amino group or groups from a di- or polyamine containing primary amino groups and having a number average molecular weight of 60 to 6000, and which  
 20 may contain further functional groups that either are reactive with isocyanate groups or are inert to isocyanate groups at temperatures of up to 100°C,

25 R<sub>5</sub> and R<sub>6</sub> may be identical or different and represent hydrogen or organic groups which are inert towards isocyanate groups at

a temperature of 100°C or less (both are preferably hydrogen),

5           R<sub>3</sub> and R<sub>4</sub> may be identical or different and represent organic groups which are inert towards isocyanate groups at a temperature of 100°C or less (preferably a C<sub>1</sub> to C<sub>8</sub> alkyl and most preferably methyl or ethyl),

10           R<sub>1</sub> and R<sub>2</sub> may be the same or different and represent moieties selected from the group consisting of i) C<sub>1</sub> to C<sub>8</sub> alkyl groups, ii) C<sub>6</sub> to C<sub>10</sub> aryl groups, which may be substituted with up to three alkyl groups having from 1 to 3 carbon atoms, iii) C<sub>6</sub> to C<sub>12</sub> cycloalkyl groups, which may be substituted with up to three alkyl groups having from 1 to 3 carbon atoms and iv)  
15           together form a six-membered cycloalkyl group, with said cycloalkyl group being substituted with from 0 to 3 alkyl groups having from 1 to 3 carbon atoms,

20           a and b represent integers of from 1 to 5, provided that the sum of a and b is from 2 to 6.

25           The products of the present invention, when combined with a polyisocyanate, have longer potlives and provide for harder coatings than aspartates of the prior art.

          The present invention also relates to a process for preparing aspartates of the above formula comprising

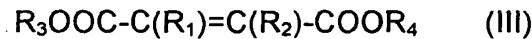
30           A)     reacting at a temperature of 0 to 100°C, in solution or in the absence of a solvent and at an equivalent ratio of primary amino groups in component a) to C=C double bonds in component b) of from about 1.1:1 to about 3.0:1

- a) di- or polyamines corresponding to formula (II)



5 with

- b) compounds corresponding to formula (III)



10 wherein

X, R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are as defined above and

m represents an integer of from 2 to 6, and

- B) reacting the resultant product with a ketone.

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The present invention also relates to a two-component coating composition which contains, as binder,

- a) a polyisocyanate component and  
b) an isocyanate-reactive component containing

20 b1) a compound corresponding to formula (I) and

b2) optionally other isocyanate-reactive compounds,

wherein the equivalent ratio of isocyanate groups to isocyanate-reactive groups is from about 0.8:1 to about 2:1, and optionally, additives known in surface coatings technology.

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Finally, the present invention also relates to prepolymers containing urea, urethane, allophanate and/or biuret structures, which are based on the reaction product of polyisocyanates with the aspartates of the invention, optionally in admixture with one or more isocyanate-reactive  
30 components.

The polyamines useful herein include i) high molecular weight amines having molecular weights of 400 to about 10,000, preferably 800 to about 6,000, and ii) low molecular weight amines having molecular weights below 400. The molecular weights are number average  
5 molecular weights ( $M_n$ ) and are determined by end group analysis (NH number). Examples of these polyamines are those wherein the amino groups are attached to aliphatic, cycloaliphatic, araliphatic and/or aromatic carbon atoms.

10            Suitable low molecular polyamine starting compounds include ethylene diamine, 1,2- and 1,3-propane diamine, 2-methyl-1,2-propane diamine, 2,2-dimethyl-1,3-propane diamine, 1,3- and 1,4-butane diamine, 1,3- and 1,5-pentane diamine, 2-methyl-1,5-pentane diamine, 1,6-hexane  
15 diamine, 2,5-dimethyl-2,5-hexane diamine, 2,2,4-and/or 2,4,4-trimethyl-1,6-hexane diamine, 1,7-heptane diamine, 1,8-octane diamine, 1,9-nonane diamine, 1,10-decane diamine, 1,11-undecane diamine, 1,12-dodecane diamine, 1-amino-3-aminomethyl-3,5,5-trimethyl cyclohexane, 2,4- and/or 2,6-hexahydrotoluylene diamine, 2,4'- and/or 4,4'-diamino-dicyclohexylmethane, 3,3'-dialkyl-4,4'-diamino-dicyclohexyl methanes  
20 (such as 3,3'-dimethyl-4,4'-diamino-dicyclohexyl methane and 3,3'-diethyl-4,4'-diamino-dicyclohexyl methane), 1,3- and/or 1,4-cyclohexane diamine, 1,3-bis(methylamino)-cyclohexane, 1,8-p-menthane diamine, hydrazine, hydrazides of semicarbazido carboxylic acids, bis-hydrazides, bis-semicarbazides, phenylene diamine, 2,4- and 2,6-toluylene diamine, 2,3-  
25 and 3,4-toluylene diamine, 2,4'- and/or 4,4'-diaminodiphenyl methane, higher functional polyphenylene polymethylene polyamines obtained by the aniline/formaldehyde condensation reaction, N,N,N-tris-(2-aminoethyl)-amine, guanidine, melamine, N-(2-aminoethyl)-1,3-propane diamine, 3,3'-diamino-benzidine, polyoxypropylene amines, polyoxy-  
30 ethylene amines, 2,4-bis-(4'-aminobenzyl)-aniline and mixtures thereof.

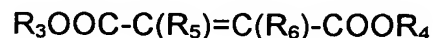
Preferred polyamines are 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane (isophorone diamine or IPDA), bis-(4-aminocyclo-hexyl)-methane, bis-(4-amino-3-methylcyclohexyl)-methane, 1,6-diamino-hexane, 2-methyl pentamethylene diamine and ethylene diamine.

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Suitable high molecular weight polyamines correspond to the polyhydroxyl compounds used to prepare the NCO prepolymers with the exception that the terminal hydroxy groups are converted to amino groups, either by amination or by reacting the hydroxy groups with a diisocyanate and subsequently hydrolyzing the terminal isocyanate group to an amino group. Preferred high molecular weight polyamines are amine-terminated polyethers such as the Jeffamine resins available from Huntsman.

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Suitable optionally substituted maleic or fumaric acid esters for use in the preparation of the aspartates are those corresponding to the formula



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wherein  $R_3$ ,  $R_4$ ,  $R_5$  and  $R_6$  are as previously defined. Examples include the dimethyl, diethyl, di-n-butyl and mixed alkyl esters of maleic acid and fumaric acid and the corresponding maleic or fumaric acid esters substituted by methyl in the 2- and/or 3-position. Suitable maleates or fumarates for preparing the aspartates of the present invention include dimethyl, diethyl, di-n-propyl, di-isopropyl, di-n-butyl and di-2-ethylhexyl maleates, methylethylmaleate or the corresponding fumarates.

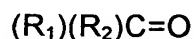
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The aspartates of the present invention are prepared by first reacting component Aa) with component Ab) at temperatures of 0 and 100°C, preferably 20 to 80°C and more preferably 20 to 60°C wherein (i)

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the equivalent ratio of primary amino groups in component a) to C=C double bond equivalents in component b) is from about 1.1:1 to about 3.0:1, preferably from about 1.1:1 to about 2.0:1. The reaction time may vary from about 1 to about 4 hours, depending upon the type of polyamine  
5 and the desired maximum residual concentration of reactants in the reaction mixture. The resultant product is then reacted with a ketone.

Useful ketones include substantially any ketone of the formula:



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where  $R_1$  and  $R_2$  are as defined above. Specifically useful ketones include acetone, methylethyl ketone, methylpropyl ketone, methylisopropyl ketone, methylisobutyl ketone, methyl n-butyl ketone, methyl sec-butyl ketone, pinacolone, methylamyl ketone, methylisoamyl ketone, methyl  
15 hexyl ketone, diethyl ketone, diisopropyl ketone, diisobutyl ketone, ethylpropyl ketone, butylethyl ketone, ethylamyl ketone, isobutylheptyl ketone, cyclopentanone, cyclohexanone, cycloheptanone, 3,3,5-trimethylcyclohexanone, diphenylketone, phenylacetone, phenylketheyyl ketone, benzylmethyl ketone and n-butyrophenone,

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This second reaction is typically conducted at a temperature of from about 50 to about 100°C, for times ranging from about 1 to about 4 hours. The ratio of reactants is chosen so that at least one mole of ketone is present for each unreacted amine group. Any excess ketone can be  
25 used to azeotropically remove the water generated when the amine reacts with the ketone. The excess ketone can then be removed to give a 100% resinous product, or it can remain and can serve as a solvent.

The process to prepare the aspartates of the present invention may  
30 either be performed in solution or in the absence of a solvent. Solvent may also be added after the synthesis process, for example, to lower the

viscosity. Suitable solvents include any organic solvents, preferably those known from surface coating technology. Examples include acetone, methyl ethyl ketone, methyl isobutyl ketone, n-butyl acetate, methoxypropyl acetate, toluene, xylene and higher aromatic solvents (such as the

5 Solvesso solvents from Exxon).

The aspartates prepared according to the invention may be directly used as reactive components for polyisocyanates after concluding the synthesis process.

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One use of the aspartates of the present invention is to prepare coatings from two-component coating compositions containing, as binder,

- a) a polyisocyanate component and
- b) an isocyanate-reactive component containing
  - 15 b1) the aspartates of the invention and
  - b2) optionally other known isocyanate-reactive components.

Suitable polyisocyanate components a) are known and include the

20 polyisocyanates known from polyurethane chemistry, e.g, low molecular weight polyisocyanates and lacquer polyisocyanates prepared from these low molecular weight polyisocyanates. Preferred are the lacquer polyisocyanates, which are known from surface coating technology. These lacquer polyisocyanates contain biuret groups, isocyanurate groups,

25 allophanate groups, uretdione groups, carbodiimide groups and/or urethane groups and are preferably prepared from (cyclo)aliphatic polyisocyanates.

Suitable low molecular weight polyisocyanates for use in

30 accordance with the present invention or for preparing the lacquer polyisocyanates are those having a molecular weight of 140 to 300, such

as 1,4- tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate (HDI), 2,2,4- and/or 2,4,4-trimethyl-hexamethylene diisocyanate, dodecamethylene diisocyanate, 2-methyl-1,5-diisocyanatopentane, 1,4-diisocyanatocyclohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanato-methylcyclohexane (IPDI), 2,4- and/or 4,4' diisocyanato-dicyclohexylmethane, 1-isocyanato-1-methyl-3(4)-isocyanatomethyl-cyclohexane (IMCI), 2,4- and/or 2,6-hexahydrotoluylene diisocyanate (H<sub>6</sub>TDI), 2,4- and/or 4,4'-diisocyanatodiphenylmethane or mixtures of these isomers with their higher homologs (which may be obtained in known manner by the phosgenation of aniline/formaldehyde condensates), 2,4- and/or 2,6-diisocyanatotoluene, and mixtures thereof. The use of low molecular weight polyisocyanates themselves is not preferred. Also, lacquer polyisocyanates prepared from aromatic polyisocyanates, such as 2,4- and/or 2,6-diisocyanatotoluene, are also less preferred. The lacquer polyisocyanates containing urethane groups are preferably based on low molecular weight polyhydroxyl compounds having molecular weights of 62 to 300, such as ethylene glycol, propylene glycol and/or trimethylolpropane.

Preferred lacquer polyisocyanates for use as component a) are those based on 1,6-hexamethylene diisocyanate and having an NCO content of 16 to 24 wt.% and a maximum viscosity at 23°C of 10,000, preferably 3,000 mPa.s.

Component b1) is selected from the aspartates of the present invention. Preferably, X represents a divalent hydrocarbon group obtained by removing the amino groups from 1-amino-3-aminomethyl-3,5,5-trimethyl-cyclohexane (isophorone diamine or IPDA), bis-(4-aminocyclo-hexyl)-methane, bis-(4-amino-3-methylcyclohexyl)-methane, 1,6-diamino-hexane, 2-methyl pentamethylene diamine and ethylene diamine.

Particularly preferred starting components b1) include those aspartates in which  $R_3$  and  $R_4$  represent  $C_1$  to  $C_8$  alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl or 2-ethylhexyl.

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Optional starting components b2) are known compounds containing at least two isocyanate-reactive groups, including groups which react with isocyanate groups under the effect of either moisture or/and heat.

Examples include hydroxy-functional polyacrylates and polyesterpolyols

10 Mixtures of these compounds may also be used.

In the binders used according to the invention, the amounts of components a), b1) and (optionally) b2) are selected such that the equivalent ratio isocyanate groups to isocyanate-reactive groups is from about 0.8:1 to about 2.0:1, and preferably from about 0.8:1 to about 1.2:1.

The binders according to the invention are prepared by mixing the individual components either in the absence of a solvent or in the presence of the solvents which are conventionally used in polyurethane surface coating technology. Suitable solvents include ethyl acetate, butyl acetate, methoxypropyl acetate, methyl isobutyl ketone, methyl ethyl ketone, xylene, N-methylpyrrolidone, petroleum spirit, chlorobenzene, Solvesso solvent or mixtures thereof.

25 Preferably, the ratio by weight of binder components a) and b) to solvent in the coating compositions according to the invention is from about 40:60 to about 100:0, more preferably from about 60:40 to about 100:0.

The coating compositions may also contain the known additives from surface coating technology. These include pigments, fillers, flow control agents, catalysts and anti-settling agents.

- 5           The properties of the coatings obtained from the coating compositions according to the invention may be adjusted by appropriate selection of the type and ratios of starting components a), b1) and b2).

10           The coating compositions may be applied to any substrate in a single layer or in several layers by known methods, e.g., by spraying, painting, immersing, flooding or by using rollers or spreaders. The coating compositions according to the invention are suitable for preparing coatings on substrates, such as metals, plastics, wood or glass. The coating compositions are especially suitable for coating steel sheeting,  
15           which is used for the production of vehicle bodies, machines, cladding panels, barrels and containers. The substrates may be provided with suitable primer coats prior to applying the coating compositions according to the invention. Drying of the coatings may take place at a temperature of about 0 to 160°C.

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          The process for producing coatings using the aspartates of the present invention may also be used for the production of prepolymers containing urea, urethane, allophanate and/or biuret structures.

- 25           The aspartates of the present invention may be directly used after completion of the synthesis process because, in contrast to prior art aspartates, an approximately complete degree of conversion is achieved. As a result of the low concentration of maleates, fumarates and primary amino groups, these products are not only toxicologically and  
30           physiologically harmless, they also exhibit a reasonable, as opposed to a vigorous, reactivity towards isocyanates. Due to their low viscosity, they

are a more than suitable alternative, as reactive diluents, to the environmentally polluting organic solvents previously used and may therefore be used in high quality, low-solvent or even solvent-free, high solids, two-component coating compositions.

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All parts and percentages in the examples which follow are by weight, unless otherwise indicated.

#### Example 1

##### 10 Preparation of a "half" aspartate:

A round bottom flask was fitted with stirrer, heating mantle, nitrogen inlet, thermocouple and addition funnel. 340 grams (4.0 eq.) of isophoronediamine (IPDA) were added to the flask at room temperature. 344 grams (2.0 eq) of diethyl maleate (DEM) were then added through the addition funnel over a period of forty-five minutes. The temperature of the flask rose to 65°C. The reaction was cooled to 60°C and held for two hours at which time the unsaturation number was 0.0 mg maleic acid per g resin indicating 100% reaction. The reaction mixture was cooled to room temperature. The amine number was 321 mg KOH/g resin (theoretical = 328).

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##### Preparation of aspartate-ketimine:

A round bottom flask was fitted with stirrer, heating mantle, nitrogen inlet, thermocouple and Dean and Stark apparatus. 264 grams (2.64 eq.) of methylisobutyl ketone (MiBK), 230 grams (1.32 eq) of the "half" aspartate prepared as above and 0.023 grams of para-toluenesulfonic acid (as catalyst) were added to the flask at room temperature. The temperature was increased to 112°C, which was the reflux temperature. After one half hour, 5.5 ml water was collected. After an additional fifteen minutes no additional water was collected, so the temperature was increased to 125°C. At this temperature, an additional 4 ml water was

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collected. After an additional two and one half hours, no additional water was collected, so the reaction was cooled to 45°C in preparation for vacuum distillation. The Dean and Stark apparatus was replaced with a vacuum connection. Distillation began at 50°C and 67 torr pressure. Over the next two hours, the temperature was increased to 80°C and the pressure reduced to 47 torr. The amine number was 245 mg KOH/g resin (theoretical = 219). A gas chromatogram showed an approximate 1:2:1 area ratio of diketimine:monoaspartate-monoketimine:diketimine with no residual starting materials.

#### Example 2 (comparative)

##### Preparation of diketimine

The diketimine is prepared in a similar procedure to that for the aspartate-ketimine. 122 grams (1.32 eq) of IPDA, 264 grams (2.64 eq) of MiBK and 0.0122 grams of para-toluenesulfonic acid (as catalyst) were mixed together at room temperature. The reaction mixture was heated to 110°C and held at that temperature for three hours over which time 16 grams of water were collected. After an additional two and one half hours, no additional water was collected, so the reaction was cooled to 50°C in preparation for vacuum distillation. The Dean and Stark apparatus was replaced with a vacuum connection. Distillation began at 50°C and 67 torr pressure. Over the next two hours, the temperature was increased to 105°C and the pressure reduced to 49 torr. The amine number of the resultant product was 336 mg KOH/g resin (theoretical = 336).

#### Example 3 (comparative)

##### Preparation of diaspartate (IPDA/DEM)

A round bottom flask was fitted with stirrer, thermocouple, addition funnel and nitrogen inlet. 127.5 grams (1.5 eq) of IPDA was added to the flask at room temperature. 258.0 grams (1.5 eq) of DEM was then added to the flask via the addition funnel over a one and one half hour period.

The temperature of the reaction mixture rose to 40°C as a result of a reaction exotherm. The reaction was held at 60°C for an additional four and one half hours. The unsaturation number was 4.7 mg maleic acid per gram of resin, which indicated 90% of the IPDA had been converted to aspartate. After eight weeks the unsaturation number was 3.96 indicating 92% conversion. The resin viscosity was 540 mPa·sec at 25°C.

#### Performance tests

Coatings were prepared by mixing a solution of 80 parts Desmodur XP-7100 (a commercially available trimer containing polyisocyanate based on HDI having an NCO content of 20% by weight, and an NCO equivalent weight of 210, from Bayer Polymers LLC) and 20 parts propylene glycol methyl ether acetate (PMA) with the resin shown at a ratio of 1.1:1 NCO:NH. The mixtures were hand mixed for about 1.5 minutes.

Potlife was determined using a #2 Zahn cup. Readings were taken every half hour until the coating viscosity reached 100 seconds (Automotive Test Method C-02).

The "cotton ball" dry time was determined by applying the formulation mixture at 3 mils wet film thickness (WFT) on glass. The dry time was checked every fifteen minutes by lightly touching the raw edge of a cotton ball to the coating until fibers no longer stuck (Automotive Test Method A-01).

Panels prepared for pendulum hardness testing were evaluated for visual clarity. Pendulum hardness was determined on a coating prepared by applying the formulation mixture at 90 microns WFT on glass. The hardness was measured on a Koenig Pendulum hardness tester when the coating had aged 1, 5, 7 and 14 days (Automotive Test Method B-01).

The formulations and the test results were as indicated in the following table:

Formulation	A	B
XP7100	69	79
PMA	35	25
Diketimine (Ex. 2)	0	42
Diaspartate (Ex. 3)	0	30
Resin from Ex. 1	71	0
Performance		
Potlife, seconds		
Initial	20	35
After 30 min	35	150
After 1 hour	65	--
After 1.5 hours	113	--
Dry Time, hours	2	2
Film clarity	clear	clear
Hardness, seconds		
1 day	149	85
5 days	155	72
7 days	146	66
14 days	160	45

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The aspartate to ketimine ratio in the monoaspartate-monoketimine was 1:1, whereas the aspartate to ketimine ratio in the physical blend was 1:2. One would expect that the formulation using the physical blend would have the longer potlife since there is more of the blocked amine in the form of ketimine present. Similarly, since there is more ketimine present in the blend, one would expect that the coating based on this material would be the harder coating since it would have the most IPDA urea present.

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Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

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